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(54) A novel protecting layer for gelatin based AGX photographic products

(57) The present invention is an imaged photographic element which includes a support, at least one silver halide light-sensitive emulsion layer superposed on the support; and a protective overcoat furthest from the support. The protective overcoat is superposed on the silver halide light sensitive layer, the protective overcoat includes a first polymeric particle having a glass transition temperature of greater than or equal to 25 °C and a particle size of from 5 to 500 nm and a second polymeric particle having a glass transition temperature of less than 25 °C and a particle size of from 5 to 500 nm at a weight ratio of the first polymeric particle to the second polymeric particle of from 3:97 to 80:20. The protective overcoat is applied from an aqueous coating.

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Description

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application relates to commonly assigned copending application Serial No. 08/965,335, filed simultaneously herewith and hereby incorporated by reference for all that it discloses.

BACKGROUND OF THE INVENTION

[0002] Silver halide photographic elements contain light sensitive silver halide in a hydrophilic emulsion. An image is formed in the element by exposing the silver halide to light, or to other actinic radiation, and developing the exposed silver halide to reduce it to elemental silver.

[0003] In color photographic elements a dye image is formed as a consequence of silver halide development by one of several different processes. The most common is to allow a by-product of silver halide development, oxidized silver halide developing agent, to react with a dye forming compound called a coupler. The silver and unreacted silver halide are then removed from the photographic element, leaving a dye image.

[0004] In either case, formation of the image commonly involves liquid processing with aqueous solutions that must penetrate the surface of the element to come into contact with silver halide and coupler. Thus, gelatin, and similar natural or synthetic hydrophilic polymers, have proven to be the binders of choice for silver halide photographic elements. Unfortunately, when gelatin, and similar polymers, are formulated so as to facilitate contact between the silver halide crystal and aqueous processing solutions, they are not as tough and mar-resistant as would be desired for something that is handled in the way that an imaged photographic element may be handled. Thus, the imaged element can be easily marked by fingerprints, it can be scratched or torn and it can swell or otherwise deform when it is contacted with liquids.

[0005] There have been attempts over the years to provide protective layers for gelatin based photographic systems that will protect the images from damage by water or aqueous solutions. US Patent No. 2,173,480 describes a method of applying a colloidal suspension to moist film as the last step of photographic processing before drying. A series of patents describes methods of solvent coating a protective layer on the image after photographic processing is completed and are described in US Patent Nos. 2,259,009, 2,331,746, 2,798,004, 3,113,867, 3,190,197, 3,415,670 and 3,733,293. The application of UV-polymerizable monomers and oligomers on processed image followed by radiation exposure to form crosslinked protective layer is described US Patent Nos. 4,092,173, 4,171,979, 4,333,998 and 4,426,431. Major drawbacks for the solvent coating method and the radiation cure method are the health and environmental concern of those chemicals to the coating operator and the instability and relatively short shelf life of the coating solutions. US Patent Nos. 3,397,980, 3,697,277 and 4,999,266 describe methods of laminating polymeric sheet film on the processed image as the protective layer. US Patent No. 5,447,832 describes the use of a protective layer containing mixture of high and low Tg latices as the water-resistance layer to preserve the antistat property of the V_2O_5 layer through photographic processing. This protective layer is not applicable to the image formation layers since it will detrimentally inhibit the photographic processing. US Patent No. 2,706,686 describes a lacquer finish for photographic emulsions, with the aim of providing water- and fingerprint-resistance by coating the emulsion, prior to exposure, with a porous layer that has a high degree of water permeability to the processing solutions. After processing, the lacquer layer is fused and coalesced into a continuous, impervious coating. The porous layer is achieved by coating a mixture of a lacquer and a solid removable extender (ammonium carbonate), and removing the extender by sublimation or dissolution during processing. The overcoat as described is coated as a suspension in an organic solvent, and thus is not compatible with current manufacturing of photographic products. US Patent No. 3,443,946 provides a roughened (matte) scratch-protective layer, but not a water-impermeable one. US Patent No. 3,502,501 provides protection against mechanical damage only; the layer in question contains a majority of hydrophilic polymeric materials, and must be permeable to water in order to maintain processability. US Patent No. 5,179,147 likewise provides a layer that is not water-protective.

[0006] In USSN 08/698,838 a protective overcoat is formed by applying a coating, in the presence of a electric field, charged, clear polymeric particles to an imaged silver halide element so as to cause the particles to adhere to a surface of the imaged element and then fusing the polymeric particles. In USSN 08/898,985 a protective overcoat is formed by applying a coating of hydrophobic polymer particles having an average size of 0.01 to 1 microns, a melting temperature of from 55 to 200 °C at a weight percent of 30 to 95, and gelatin at a weight percent of 5 to 70 over a silver halide light-sensitive emulsion layer. The silver halide light sensitive emulsion layer is developed to provide an imaged photographic element. The hydrophobic polymer particles are then fused to form a protective overcoat. However, there remains a need to provide protective overcoats on photographic elements without a fusing step.

[0007] The temperature and residence time of photographic coating in the drying section of photofinishing equipment in the trade vary from 50 °C to 70 °C and from 30 seconds to 2.5 minutes. The actual temperature of gelatin coating during drying is much lower than the temperature set for the dryer due to the evaporation of water. In addition, it is necessary to be free of volatile organic compound (VOC) in the formulation to be user and environmental friendly. Under these stringent requirements, it appears that an aqueous colloidal dispersion of a water insoluble polymeric material is an appropriate system for this technology. Water soluble materials will not provide any water resistance property.

[0008] US Patent No. 2,719,791 describes the use of an aqueous dispersion of organic plastic material, which yields a water impermeable coating on drying. However, it is known that when dispersions of low Tg (glass transition temperature) material (Tg<25 °C) are used to obtain a water resistance protective coating, the surface of the protective coating has an undesirable tacky characteristic, which generally degrades other physical properties, such as print blocking, fingerprinting, dust attraction and high scratch propensity. When dispersions of high Tg materials (Tg>25 °C) are used, it is not possible to form a continuous water resistance layer on the prints under the drying condition described above. US Patent No. 2,751,315 also describes the use of an aqueous dispersion of copolymer materials. It was recognized in this patent that low Tg materials were not suitable and therefore higher Tg polymers in combination with an organic solvent were used in order to form a water-resistant protective coating. The organic solvent that is released from the formulation during drying creates an environmental concern if used in the current photofinishing laboratories. US Patent No. 2,956,877 describes a method of applying a solution to a photographic image that solublizes the processing reagents from the photographic products as well as forming a protective coating on its surface. The acid groups on the polymer degrades the water resistant property of the final protective layer, and the organic solvent required in the formulation is not suitable for high volume photofinishing laboratories.

[0009] There remains a need for an aqueous coatable, water-resistant protective coating having excellent physical handling characteristics, that can be easily coated on imaged processed photographic products, dried into a continuous layer under drying conditions typical of photographic processing equipment, while not releasing volatile organic compounds.

SUMMARY OF THE INVENTION

[0010] The present invention is an imaged photographic element which includes a support, at least one silver halide light-sensitive emulsion layer superposed on the support; and a protective overcoat furthest from the support. The protective overcoat is superposed on the silver halide light sensitive layer. The protective overcoat includes a first polymeric particle having a glass transition temperature of greater than or equal to 25 °C and a particle size of from 5 to 500 nm and a second polymeric particle having a glass transition temperature of less than 25 °C and a particle size of from 5 to 500 nm at a weight ratio of the first polymeric particle to the second polymeric particle of from 3:97 to 80:20. The protective overcoat is applied from an aqueous coating.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The present invention describes a volatile organic-solvent-free material formulation that is applied to a photographic product at the end of photographic processing and dried to form a water resistant, scratch resistant durable overcoat. The material composition of this invention is a combination of two colloidal dispersions of water insoluble hydrophobic polymeric materials. At least one of the polymeric materials has glass transition temperature equal to or higher than 25 °C to provide toughness and non-tacky surface properties. The second polymeric material has glass transition temperature below 25 °C in order to form a continuous film layer at the mild drying condition, such as used in typical photographic processing equipment. The weight ratio of the two polymeric materials is from 3:97 to 80:20 by weight. The average particle size of colloidal dispersions of polymeric materials is from 5 nm to 500 nm. The dry laydown of the total materials on the surface of photographic product is from 0.3 g/m^2 to 6 g/m^2. Other components commonly used in photographic processing solutions, such as biocides, spreading aids (surfactants), and lubricants can also be incorporated in the formulation as needed. The concentration of the formulation can be from 1% total solids to 50% total solids depending on the desired thickness of the protective layer, the machine speed, the dryer efficiency and other factors that may affect the application to the photographic product.

[0012] The colloidal dispersions of hydrophobic polymers used for the first or second polymeric particle in the present invention are generally latexes or hydrophobic polymers of any composition that can be stabilized in an water-based medium. Such hydrophobic polymers are generally classified as either condensation polymers or addition polymers. Condensation polymers include, for example, polyesters, polyamides, polyurethanes, polyureas, polyethers, polycarbonates, polyacid anhydrides, and polymers comprising combinations of the above-mentioned types. Addition polymers are polymers formed from polymerization of vinyl-type monomers including, for example, allyl compounds, vinyl ethers, vinyl esters, vinyl heterocyclic compounds, styrenes, olefins and halogenated olefins, unsaturated acids and esters derived from them, unsaturated nitriles, vinyl alcohols, acrylamides and methacrylamides, vinyl ketones, multifunctional monomers, or copolymers formed from various combinations of these monomers. Such latex polymers can be prepared in aqueous media using well-known free-radical emulsion polymerization methods and may consist of homopolymers made from one type of the above-mentioned monomers or copolymers made from more than one type of the above-mentioned monomers. Polymers comprising monomers which form water-insoluble homopolymers are preferred, as are copolymers of such monomers. Preferred polymers may also comprise monomers which give water-soluble homopolymers, if the overall polymer composition is sufficiently water-insoluble to form a latex. The aqueous phase of the latex or colloidal dispersion of the invention may contain water-soluble polymers in order to control, for example, the viscosity and flow characteristics. The aqueous phase may also include surfactants of the cationic, anionic, zwitterionic or non-ionic types. Further listings of suitable monomers for addition type polymers are found in US Patent No. 5,594,047 incorporated herein by reference.

[0013] The photographic products according to the present invention have the unique features of water resistance, improved scratch resistance and improved thermal blocking performance. In addition, volatile organic solvents or compounds are not released from the formulation.

[0014] The imaged photographic elements protected in accordance with this invention are derived from silver halide photographic elements that can be black and white elements (for example, those which yield a silver image or those which yield a neutral tone image from a mixture of dye forming couplers), single color elements or multicolor elements. Multicolor elements typically contain dye image-forming units sensitive to each of the three primary regions of the spectrum. The imaged elements can be imaged elements which are viewed by transmission, such a negative film images, reversal film images and motion picture prints or they can be imaged elements that are viewed by reflection, such a paper prints. Because of the amount of handling that can occur with paper prints and motion picture prints, they are preferred imaged photographic elements for use in this invention.

[0015] The photographic elements in which the images to be protected are formed can have the structures and components shown in Research Disclosure 37038. Specific photographic elements can be those shown on pages 96-98 of Research Disclosure 37038 as Color Paper Elements 1 and 2. A typical multicolor photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers, subbing layers, and the like. All of these can be coated on a support which can be transparent (for example, a film support) or reflective (for example, a paper support). Photographic elements protected in accordance with the present invention may also include a magnetic recording material as described in Research Disclosure, Item 34390, November 1992, or a transparent magnetic recording layer such as a layer containing magnetic particles on the underside of a transparent support as described in US 4,279,945 and US 4,302,523.

[0016] Suitable silver halide emulsions and their preparation, as well as methods of chemical and spectral sensitization, are described in Sections I through V of Research Disclosure 37038. Color materials and development modifiers are described in Sections V through XX of Research Disclosure 37038. Vehicles are described in Section II of Research Disclosure 37038, and various additives such as brighteners, antifoggants, stabilizers, light absorbing and scattering materials, hardeners, coating aids, plasticizers, lubricants and matting agents are described in Sections VI through X and XI through XIV of Research Disclosure 37038. Processing methods and agents are described in Sections XIX and XX of Research Disclosure 37038, and methods of exposure are described in Section XVI of Research Disclosure 37038.

[0017] Photographic elements typically provide the silver halide in the form of an emulsion. Photographic emulsions generally include a vehicle for coating the emulsion as a layer of a photographic element. Useful vehicles include both naturally occurring substances such as proteins, protein derivatives, cellulose derivatives (e.g., cellulose esters), gelatin (e.g., alkali-treated gelatin such as cattle bone or hide gelatin, or acid treated gelatin such as pigskin gelatin), gelatin derivatives (e.g., acetylated gelatin, phthalated gelatin, and the like). Also useful as vehicles or vehicle extenders are hydrophilic water-permeable colloids. These include synthetic polymeric peptizers, carriers, and/or binders such as poly(vinyl alcohol), poly(vinyl lactams), acrylamide polymers, polyvinyl acetals, polymers of alkyl and sulfoalkyl acrylates and methacrylates, hydrolyzed polyvinyl acetates, polyamides, polyvinyl pyridine, methacrylamide copolymers, and the like.

[0018] Photographic elements can be imagewise exposed using a variety of techniques. Typically exposure is to light in the visible region of the spectrum, and typically is of a live image through a lens. Exposure can also be to a stored image (such as a computer stored image) by means of light emitting devices (such as LEDs, CRTs, etc.).

[0019] Images can be developed in photographic elements in any of a number of well known photographic processes utilizing any of a number of well known processing compositions, described, for example, in T.H. James, editor, The Theory of the Photographic Process, 4th Edition, Macmillan, New York, 1977. In the case of processing a color negative element, the element is treated with a color developer (that is one which will form the colored image dyes with the color couplers), and then with an oxidizer and a solvent to remove silver and silver halide. In the case of processing a color reversal element, the element is first treated with a black and white developer (that is, a developer which does not form colored dyes with the coupler compounds) followed by a treatment to render developable unexposed silver halide (usually chemical or light fogging), followed by treatment with a color developer. Development is followed by bleach-fixing, to remove silver or silver halide, washing and drying.

[0020] The present invention is illustrated by the following examples.

Examples

Material preparation:

S4

[0021] To a 1L three-necked reaction flask fitted with a stirrer and condenser was added 300 ml of degassed distilled water, 2 ml of 45% Dowfax 2A1 (available from Dow Chemical Company), 1.00 g of potassium persulfate, and 0.33 g of sodium metabisulfite. The flask was placed in a 60 °C bath and the contents of an addition flask containing 100 ml of distilled water, 2 ml of 45% Dowfax 2A1, 15 g of methyl acrylate, 83 g of 2-chloroethyl acrylate, and 2 g of itaconic acid was added to the reaction flask over a period of 40 minutes. The reaction flask was stirred at 80 °C for 1 hour and 0.25 g of potassium persulfate was added and the contents stirred at 80 °C for additional 90 minutes. The flask was cooled and the pH of the latex was adjusted to 5.5 using 10% sodium hydroxide to give a latex containing 19.1% solids. The Tg of the polymer was 4 °C.

H3

[0022] This latex was prepared in a similar way as for sample S4, except the monomer mixture consists of 95 g of n-butyl methacrylate and 5 g of 2-sulfo-1,1-dimethylethyl acrylamide (sodium salt).

H4

[0023] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 50 g of methyl methacrylate, 48 g of 2-chloroethyl acrylate, and 2 g of itaconic acid.

H6

[0024] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 60 g of ethyl methacrylate and 40 g of 2-chloroethyl acrylate

H7

[0025] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 75 g of ethyl methacrylate and 25 g of 2-chloroethyl acrylate.

H12

[0026] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 75 g of methyl methacrylate and 25 g of 2-chloroethyl acrylate.

S3

[0027] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 15 g of ethyl methacrylate, 83 g of 2-chloroethyl acrylate, and 2 g of itaconic acid.

S5

[0028] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 17 g of methyl acrylate and 83 g of 2-chloroethyl acrylate.

S6

[0029] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 15 g of n-butyl methacrylate, 83 g of 2-chloroethyl acrylate, and 2 g of itaconic acid.

S7

[0030] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 30 g of n-butyl methacrylate, 68 g of 2-chloroethyl acrylate, and 2 g of itaconic acid.

S8

[0031] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 50 g of n-butyl methacrylate, 48 g of 2-chloroethyl acrylate, and 2 g of itaconic acid.

S9

[0032] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 25 g of ethyl methacrylate and 75 g of 2-chloroethyl acrylate.

S10

[0033] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 40 g of ethyl methacrylate and 60 g of 2-chloroethyl acrylate.

H1

[0034] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 15 g of methylacrylate, 83 g of vinylidene chloride and 2 g of itaconic acid.

H2

[0035] This latex was prepared in a similar way as for sample S4, except the monomer mixture consisted of 15 g of acrylonitrile, 79 g of vinylidene chloride and 6 g of acrylic acid.

S13 (polyester)

[0036] Dimethyl-1,4-cyclohexanedicarboxylate (44 g), dimethyl-5-sulfoisophthalate (8.9 g), 1,4-cyclohexanedimethanol (27.3 g) and decanediol (10.5 g) were weighed into a 250 mL round-bottom, long-necked flask. A take-off arm was attached to the top of the flask. Under a nitrogen stream the monomers were first melted at 250 °C, then the molten monomers were purged with nitrogen. Antimonypentoxide, 0.5 mL of a 6% dispersion in ethylene glycol was added. Five drops of neat titanium isopropoxide were added, and the resulting methanol distillate was collected. After two hours, a vacuum manifold and a stir paddle was attached to the flask, and a vacuum applied with stirring. The reaction continued for two hours under vacuum. The flask was then allowed to cool to room temperature for 30 minutes, before the vacuum was released. Polymers was isolated by freezing the flask in liquid nitrogen and breaking the flask. The polymer had a Tg of 17 °C. The polymer dispersion was obtained by stirring the solid polymer in 80 °C water for 14 hours.

S11 (polyamide-ester)

[0037] A polyamide oligomer was prepared by weighting dimethyl-1,4-cyclohexanedicarboxylate (100 g) and hexamethylenediamine (57 g) into a 250 mL round-bottom, long-necked flask. A take-off arm was attached to the top of the flask. Under a nitrogen stream the monomers were melted at 250 °C, then the molten monomers were purged with nitrogen, and then heated under nitrogen for one hour. A vacuum manifold and a stir paddle was attached to the flask, and a vacuum applied with stirring. The reaction continued for two hours under vacuum. The flask was then allowed to cool to room temperature for 30 minutes, before the vacuum was released. Polymers were isolated by freezing the flask in liquid nitrogen and breaking the flask. The polyamide oligomer (7.14 g) was weighed into a 250 mL round-bottom, long-necked flask, and the procedure described above for S13 was followed, using 40 grams dimethyl-1,4-cyclohexanedicarboxylate, 11.8 g dimethyl-5-sulfoisophthalate, 24.5 g 1,4-cyclohexanedimethanol and 14.0 g decanediol. The resulting polyamide-ester had a Tg of 20 °C. The polymer dispersion was obtained by stirring the solid polymer in 80 °C water for 14 hours.

Others

[0038] Commercially available materials were dialyzed against distilled water for 16 hours using membrane with molecular weight cutoff of 20,000 to remove organic solvent and excess surfactants and salts.

Glass Transition Temperature (Tg)

[0039] The glass transition temperature (Tg) of the dry polymer material was determined by differential scanning calorimetry (DSC), using a ramping rate of 20 °C/minute. Tg is defined herein as the inflection point of the glass transition. The glass transition temperatures of materials used in this invention are listed in Table 1 below.

Particle Size Measurement

[0040] All particles were characterized by Photon Correlation Spectroscopy using a Zetasizer Model DTS5100 manufactured by Malvern Instruments. Sizes are reported as Z averages.

Table 1

ID	Name	Source	Material Class	Tg (°C)	Particle Size (mm)
H1		Kodak	Vinylidene chloride copolymer	25	99
H2		Kodak	Vinylidene chloride copolymer	46	97
H3		Kodak	Acrylate copolymer	35	60
H4		Kodak	Acrylate copolymer	48	75
H5	LL990	Wacker	Acrylate copolymer	73	73
H6		Kodak	Acrylate copolymer	31	68
H7		Kodak	Acrylate copolymer	40	75
H8	Flexthane 620	Air Product	Polyurethane		114
H9	Flexthane 790	Air Product	Polyurethane		101
H10	Flexthane 791	Air Product	Polyurethane	56 (very broad transition)	91
H11	Joncryl 537	SC Johnson	Acrylic emulsion polymer		74
H12		Kodak	Acrylate copolymer	79	75
H13	Joncryl 2161	SC Johnson	Acrylic emulsion polymer	90	138
H14	Joncryl ECO2189	SC Johnson	Acrylic emulsion polymer	98	109
H15	Joncryl 1603	SC Johnson	Acrylic emulsion polymer	25	85
S2	LL970	Wacker	Acrylate copolymer	5	79
S3		Kodak	Acrylate copolymer	10	74
S4		Kodak	Acrylate copolymer	4	76
S5		Kodak	Acrylate copolymer	7	75
S6		Kodak	Acrylate copolymer	4	80
S7		Kodak	Acrylate copolymer	5	64

Table 1 (continued)

ID	Name	Source	Material Class	Tg (°C)	Particle Size (mm)
S8		Kodak	Acrylate copolymer	9	59
S9		Kodak	Acrylate copolymer	10	117
S10		Kodak	Acrylate copolymer	15	85
S11		Kodak	Polyamide-ester	20	232
S12	Joncryl HR1663	SC Johnson	Acrylic emulsion polymer	-55	120
S13		Kodak	Polyester	17	156
S14	Joncryl 1645	SC Johnson	Acrylic emulsion polymer	15	163

Sample Preparation:

[0041] All samples were prepared by coating aqueous colloidal dispersions on the unexposed/processed (Dmin) Kodak Edge 5 Ektacolor paper at 3cc/sq.ft with dryer temperature @140 °F to simulate a tail-end of photofinishing process. Small amounts of FT-248, an anionic fluorosurfactant available from Bayer AG (used at 0.1% to 4% based on the total dry laydown of the layer, other surface active compounds can also be used), and ME39235 (polyethylene particles of 40 nm, available from Michelman, used at 0% to 40% based on the total dry laydown of the layer) were used in the formulation to control the surface tension and coefficient of friction.

Test for Water Resistance

[0042] Ponceau Red dye is known to stain gelatin through ionic interaction. Ponceau red dye solution was prepared by dissolving 1 gram dye in 1000 grams mixture of acetic acid and water (5 parts: 95 parts). Samples were soaked in the dye solution for 5 minutes followed by a 30-second water rinse to removed excess dye solution on the coating surface, then air dried. A sample with good water resistant protective layer did not change appearance by the test. Samples showed very dense red color if there was no protective overcoat applied to the surface or the formulation did not form a continuous overcoat layer under the drying condition specified above to provide water resistance property.

Test for Durability on Wet Wiping

[0043] An approximately 1 cm-diameter Ponceau Red dye solution was placed on the sample surface for 5 minutes. The liquid was then wiped up with Sturdi-Wipes paper towel with approx. 1000 grams weight applied on it. Several phenomena were often observed.

A: no evidence of surface scratches was observed.
B: very mild scratches on the protective overcoat layer were observed.
C: very severe scratches on the protective overcoat layer were observed.
D: protective overcoat layer was removed by wiping and Ponceau red dye penetrated into image layers to give a red mark.

[0044] A visual observation was recorded. "A" is most desirable and "B" is acceptable. A result of "C" or "D" is not acceptable at all.

Test for Dry Scratch Resistance

[0045] Each sample was rubbed with a dry paper towel for 40 passes under a pressure of 0.75 psi (500 grams over a 1.375 inch-diameter area). The reduction of 20-degree gloss of the abraded area relative to the unabraded surface was recorded using a Gardner Micro-tri-gloss Meter at a measuring angle of 20 degrees. Scratches generated by the rubbing test result in a decrease in gloss reading

Test for Thermal Blocking

[0046] 3.5x4 sq. in. samples were placed face-to-face (the overcoat layer of one Sample being in contact with the sale overcoat of the other sample) in 50%RH/60 °C chamber for 6 hours with 1000 grams weight placed on top of the samples. The samples were pulled apart and evaluated according to the following scale:

10	no adhesion, no tack
9	very slight tack (aural observation)
8	slight tack (aural observation)
7	slight picking (visual observation)
6	moderate picking
5	significant picking
4	0-25% coating removal
3	25-50% coating removal
2	50-75% coating removal
1	100% coating removal (i.e. complete failure)

A ranking of 10 is most desirable, a ranking of 7 to 9 is also acceptable.

Example 1

[0047] A series of samples were prepared with the protective overcoat formulation described in Table 2.

Table 2

Sample ID	Latex of Tg>/=25°C (mg/sq.ft.)	Latex of Tg<25°C (mg/sq.ft.)	Comment
Edge 5 without protective layer			**Comparison**
1	H2 (@ 200)		comparison
2	H3 (@ 200)		Comparison
3	H4 (@ 200)		comparison
4	H6 (@ 200)		comparison
5	H8 (@ 200)		comparison
6	H9 (@ 200)		comparison
7	H10 (@ 200)		comparison
8	H15 (@ 200)		Comparison
9		S1 (@ 200)	comparison
10		S2 (@ 200)	comparison
11		S3 (@ 200)	comparison
12		S4 (@ 200)	comparison
13		S5 (@ 200)	comparison
14		S6 (@ 200)	comparison
15		S9 (@ 200)	comparison
16		S10 (@ 200)	comparison
17		S11 (@ 200)	comparison
18		S11 (@ 200)	comparison
19		S13 (@ 200)	comparison
20	H1 (@ 140)	S1 (@ 60)	**Invention**
21	H1 (@ 120)	S1 (@ 80)	**Invention**
22	H1 (@ 100)	S1 (@ 100)	**Invention**
23	H2 (@ 20)	S1 (@ 180)	**Invention**
24	H2 (@ 40)	S1 (@ 160)	**Invention**
25	H2 (@ 100)	S1 (@ 100)	**Invention**
26	H2 (@ 100)	S2 (@ 100)	**Invention**
27	H2 (@ 110)	S2 (@ 90)	**Invention**
28	H2 (@ 120)	S2 (@ 80)	**Invention**
29	H2 (@ 85)	S3 (@ 115)	**Invention**
30	H2 (@ 100)	S10 (@ 100)	**Invention**
31	H2 (@ 80)	S10 (@ 120)	**Invention**
32	H2 (@ 70)	S13 (@ 130)	**Invention**
33	H2 (@ 60)	S14 (@ 140)	**Invention**
34	H2 (@ 80)	S14 (@ 120)	**Invention**
35	H4 (@ 100)	S2 (@ 100)	**Invention**
36	H4 (@ 110)	S2 (@ 90)	**Invention**
37	H4 (@ 120)	S2 (@ 80)	**Invention**
38	H4 (@ 100)	S3 (@ 100)	**Invention**
39	H4 (@ 110)	S3 (@ 90)	**Invention**
40	H4 (@ 100)	S10 (@ 100)	**Invention**
41	H4 (@ 70)	S13 (@ 130)	**Invention**
42	H5 (@ 70)	S13 (@ 130)	**Invention**
43	H6 (@ 100)	S1 (@ 100)	**Invention**
44	H6 (@ 100)	S3 (@ 100)	**Invention**
45	H6 (@ 110)	S3 (@ 90)	**Invention**

Sample ID	Latex of Tg>/=25°C (mg/sq.ft.)	Latex of Tg<25°C (mg/sq.ft.)	Comment
47	H7 (@ 75)	S1 (@ 125)	**Invention**
48	H7 (@ 100)	S10 (@ 100)	**Invention**
49	H7 (@ 70)	S10 (@ 130)	**Invention**
50	H9 (@ 70)	S13 (@ 130)	**Invention**
51	H10 (@ 50)	S10 (@ 150)	**Invention**
52	H10 (@ 70)	S13 (@ 130)	**Invention**
53	H11 (@ 70)	S13 (@ 130)	**Invention**
54	H12 (@ 60)	S1 (@ 140)	**Invention**
55	H12 (@ 100)	S2 (@ 100)	**Invention**
56	H12 (@ 115)	S2 (@ 85)	**Invention**
57	H12 (@ 85)	S10 (@ 115)	**Invention**
58	H12 (@ 80)	S10 (@ 120)	**Invention**
59	H12 (@ 70)	S10 (@ 130)	**Invention**
60	H12 (@ 60)	S14 (@ 140)	**Invention**
61	H12 (@ 80)	S14 (@ 120)	**Invention**
62	H13 (@ 60)	S14 (@ 140)	**Invention**
63	H13 (@ 80)	S14 (@ 120)	**Invention**
64	H14 (@ 60)	S14 (@ 140)	**Invention**
65	H15 (@ 100)	S1 (@ 100)	**Invention**
66	H15 (@ 80)	S14 (@ 120)	**Invention**

[0048] The water resistance test was done on all samples, followed by wet rub durability test and dry scratch resistance test if sample showed water resistance performance. The results are shown in Table 3 below.

Table 3

Sample ID	Comment	Water Resistance	Durability on wet wiping	Gloss Loss on Dry Scratch
Edge5 without Protective layer of this invention	**Comparison**	**No**	**D**	**-4%**
1	comparison	No		
2	Comparison	No		
3	comparison	No		-4%
4	comparison	No		0%
5	comparison	No		-3%
6	comparison	No		0%
7	comparison	No		0%
8	Comparison	yes	A	-43%
9	comparison	yes	C	
10	comparison	yes	A	-14%

11	comparison	yes	A	-1%
12	comparison	yes	A	0%
13	comparison	yes	B	-3%
14	comparison	yes	A	-18%
15	comparison	yes	B	
16	comparison	yes	A	-3%
17	comparison	yes	A	-2%
18	comparison	yes	A	0%
19	comparison	yes	C	-5%
20	**Invention**	yes	A	-1%
21	**Invention**	yes	A	0%
22	**Invention**	yes	A	0%
23	**Invention**	yes	B	0%
24	**Invention**	yes	A	-1%
25	**Invention**	yes	A	-1%
26	**Invention**	yes	B	0%
27	**Invention**	yes	A	-1%
28	**Invention**	yes	A	-1%
29	**Invention**	yes	B	0%
30	**Invention**	yes	A	0%
31	**Invention**	yes	A	0%
32	**Invention**	yes	B	0%
33	**Invention**	yes	A	0%
34	**Invention**	yes	A	0%
35	**Invention**	yes	B	0%
36	**Invention**	yes	B	-2%
37	**Invention**	yes	A	-1%
38	**Invention**	yes	B	-1%
39	**Invention**	yes	A	0%
40	**Invention**	yes	A	0%
41	**Invention**	yes	B	0%
42	**Invention**	yes	B	0%
43	**Invention**	yes	B	0%
44	**Invention**	yes	B	-1%
45	**Invention**	yes	A	0%
46	**Invention**	yes	A	-1%

47	**Invention**	yes	B	
48	**Invention**	yes	B	
49	**Invention**	yes	B	-2%
50	**Invention**	yes	A	0%
51	**Invention**	yes	B	0%
52	**Invention**	yes	A	0%
53	**Invention**	yes	B	0%
54	**Invention**	yes	B	0%
55	**Invention**	yes	A	0%
56	**Invention**	yes	B	0%
57	**Invention**	yes	B	0%
58	**Invention**	yes	B	0%
59	**Invention**	yes	B	-1%
60	**Invention**	yes	A	0%
61	**Invention**	yes	A	-1%
62	**Invention**	yes	B	
63	**Invention**	yes	C	
64	**Invention**	yes	A	0%
65	**Invention**	yes	A	0%
66	**Invention**	yes	A	0%

[0049] As shown in Table 3, water resistance property can not be obtained if latex of Tg higher than 25 °C was used alone, and poor wet wiping durability and dry scratch resistance were observed when latex of Tg lower than 25 °C was used alone. Noticeable improvements on water resistance, wet wiping durability and dry scratch resistance were achieved when formulation of this invention was used for the protective layer.

Example 2

[0050] Selected samples from Example 1 were tested for thermal blocking following the procedure described previously. The results are shown in Table 4 below.

Table 4

Sample ID	Latex of Tg>/=25°C (mg/sq.ft.)	Latex of Tg<25°C (mg/sq.ft.)	Comment	60C/50%RH/6 hrs thermal blocking test
Edge 5 without protective layer			**Comparison**	**ranking=10**
9		S1 (@ 200)	comparison	ranking=6
25	H2 (@ 100)	S1 (@ 100)	**Invention**	ranking=7
43	H6 (@ 100)	S1 (@ 100)	**Invention**	ranking=7-8
10		S2 (@ 200)	comparison	ranking=7

Table 4 (continued)

Sample ID	Latex of Tg>/=25°C (mg/sq.ft.)	Latex of Tg<25°C (mg/sq.ft.)	Comment	60C/50%RH/6 hrs thermal blocking test
Edge 5 without protective layer			**Comparison**	**ranking=10**
56	H12 (@ 115)	S2 (@ 85)	**Invention**	ranking=7-8
12		S4 (@ 200)	comparison	ranking=5
13		S5 (@ 200)	comparison	ranking=3
14		S6 (@ 200)	comparison	ranking=4
15		S9 (@ 200)	comparison	ranking=5
16		S10 (@ 200)	comparison	ranking=5
40	H4 (@ 100)	S10 (@ 100)	**Invention**	ranking=7
17		S11 (@ 200)	comparison	ranking=3-4
18		S11 (@ 200)	comparison	ranking=3
19		S13 (@ 200)	comparison	ranking=4
32	H2 (@ 70)	S13 (@ 130)	**Invention**	ranking=4
41	H4 (@70)	S13 (@ 130)	**Invention**	ranking=3
42	H5 (@ 70)	S13 (@ 130)	**Invention**	ranking=4
50	H9 (@ 70)	S13 (@ 130)	**Invention**	ranking=4
52	H10 (@70)	S13 (@ 130)	**Invention**	ranking=4
53	H11 (@70)	S13 (@ 130)	**Invention**	ranking=4
34	H2 (@ 80)	S14 (@ 120)	**Invention**	ranking=7
39	H4 (@ 110)	S3 (@90)	**Invention**	ranking=7
45	H6 (@ 110)	S3 (@ 90)	**Invention**	ranking=7
46	H6 (@ 120)	S3 (@ 80)	**Invention**	ranking=7
62	H13 (@ 60)	S14 (@ 140)	**Invention**	ranking=7
63	H13 (@ 80)	S14 (@ 120)	**Invention**	ranking=8
64	H14 (@ 60)	S14 (@ 140)	**Invention**	ranking=7
66	H15 (@ 80)	S14 (@ 120)	**Invention**	ranking=8

[0051] It is well known that glass transition temperature of gelatin increases as the temperature of the environment goes up due to the dehydration of gelatin, and therefore thermal blocking at high temperature is never a concern for gelatin coating. However, the glass transition temperature of most hydrophobic polymers are not affected by the moisture or temperature of the environment, and therefore blocking is a common problem with the use of low Tg polymers at high temperature. It is shown in Table 4 that thermal blocking is a severe concern when low Tg materials are used alone in the formulation for protective layer even though they have superior water resistance performance. The formulation of this invention can reduce the thermal blocking defect as shown by the higher ranking. Comparing Sample 16 against sample 40 shows that a high Tg polymer particle in combination with a low Tg polymer particle results in improved performance relative to using a low Tg polymer alone. Comparing Sample 9 against sample 43 shows that a high Tg polymer particle in combination with a low Tg polymer particle results in improved performance relative to using a low Tg polymer alone.

[0052] The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

1. An imaged photographic element having a protective overcoat thereon, the protective overcoat formed by the steps comprising;

   providing an imaged photographic element having at least one silver halide light-sensitive emulsion layer;
   applying an aqueous coating comprising a colloidal dispersion of a first polymeric particle having a glass transition temperature of greater than or equal to 25 °C and a particle size of from 5 to 500 nm and a second polymeric particle having a glass transition temperature of less than 25 °C and a particle size of from 5 to 500 nm over the at least one silver halide light-sensitive emulsion layer wherein a weight ratio of the first polymeric particle to the second polymeric particle is from 3:97 to 80:20; and
   drying the aqueous coating to provide an imaged photographic element having a protective overcoat.

2. The imaged photographic element having the protective overcoat of claim 1 wherein the aqueous coating has a solids concentration of from 1 to 50 percent.

3. The imaged photographic element having the protective overcoat of claim 1 wherein the first polymeric material comprises a polymer selected from the group consisting of polyesters, polyamides, polyurethanes, polyureas, polyethers, polycarbonates, polyacid anhydrides and addition polymers.

4. The imaged photographic element having the protective overcoat of claim 1 wherein the second polymeric material comprises a polymer selected from the group consisting of polyesters, polyamides, polyurethanes, polyureas, polyethers, polycarbonates, polyacid anhydrides and addition polymers.

5. The imaged photographic element having the protective overcoat of claim 1 wherein the imaged photographic element is a photographic image on a transparent support.

6. The imaged photographic element having the protective overcoat of claim 1 wherein the imaged photographic element is a photographic image on a reflective support.

7. The imaged photographic element having the protective overcoat of claim 1 wherein the aqueous coating further comprises biocides, surfactants and lubricants.

8. An imaged photographic element comprising:

   a support;
   at least one silver halide light-sensitive emulsion layer superposed on the support; and
   protective overcoat furthest from the support superposed on the at least one silver halide light sensitive layer comprising a first polymeric particle having a glass transition temperature of greater than or equal to 25 °C and a particle size of from 5 to 500 nm and a second polymeric particle having a glass transition temperature of less than 25 °C and a particle size of from 5 to 500 nm at a weight ratio of the first polymeric particle to the second polymeric particle of from 3:97 to 80:20.

9. The imaged photographic element having the protective overcoat of claim 8 wherein the first polymeric material comprises a polymer selected from the group consisting of polyesters, polyamides, polyurethanes, polyureas, polyethers, polycarbonates, polyacid anhydrides and addition polymers.

10. The imaged photographic element having the protective overcoat of claim 8 wherein the second polymeric material comprises a polymer selected from the group consisting of polyesters, polyamides, polyurethanes, polyureas, polyethers, polycarbonates, polyacid anhydrides and addition polymers.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 3594

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X Y	US 5 643 972 A (WANG ET AL.) 1 July 1997 * column 2, line 9 - line 14 * * column 2, line 33 - line 39 * * column 2, line 47 - line 54 * * column 3, line 15 - line 21 * * column 5, line 34 - line 38 * * column 5, line 66 - column 6, line 1 * * column 6; table 1 * * column 7; table 2 * ---	8-10 1-7	G03C1/76 G03C11/08
X Y	US 4 822 727 A (ISHIGAKI ET AL.) 18 April 1989 * column 2, line 61 - column 3, line 4 * * column 18, line 56 - line 61 * * column 21, line 22 - line 26 * * column 23, line 15 - line 20 * * column 25; table 1 * * column 27; table 2 * * claims 1,3-6,12,14 * ---	8-10 1-7	
Y	GB 482 204 A (I.G.FARBENINDUSTRIE) * page 1, line 75 - line 82; claim 1 * ---	1-7	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)**
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 December 1998	Magrizos, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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